

Chapter 05

Lecture Outline

See separate *Image PowerPoint* slides for all figures and tables pre-inserted into PowerPoint without notes.

Chapter 5

Gases and the Kinetic-Molecular Theory



Gases and the Kinetic Molecular Theory

5.1 An Overview of the Physical States of Matter

5.2 Gas Pressure and Its Measurement

5.3 The Gas Laws and Their Experimental Foundations

5.4 Rearrangements of the Ideal Gas Law

5.5 The Kinetic-Molecular Theory: A Model for Gas Behavior



An Overview of the Physical States of Matter

Distinguishing gases from liquids and solids.

- Gas volume changes significantly with pressure.
 - Solid and liquid volumes are not greatly affected by pressure.
- Gas volume changes significantly with temperature.
 - Gases expand when heated and shrink when cooled.
 - The volume change is 50 to 100 times greater for gases than for liquids and solids.
- Gases flow very freely.
- Gases have relatively low densities.
- Gases form a solution in any proportions.
 - Gases are freely miscible with each other.



Figure 5.1 The three states of matter.

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Gas: Particles are far apart, move freely, and fill the available space.

Liquid: Particles are close together but move around one another.

Solid: Particles are close together in a regular array and do not move around one another.

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Gas Pressure and its Measurement

$$\text{Pressure} = \frac{\text{force}}{\text{area}}$$

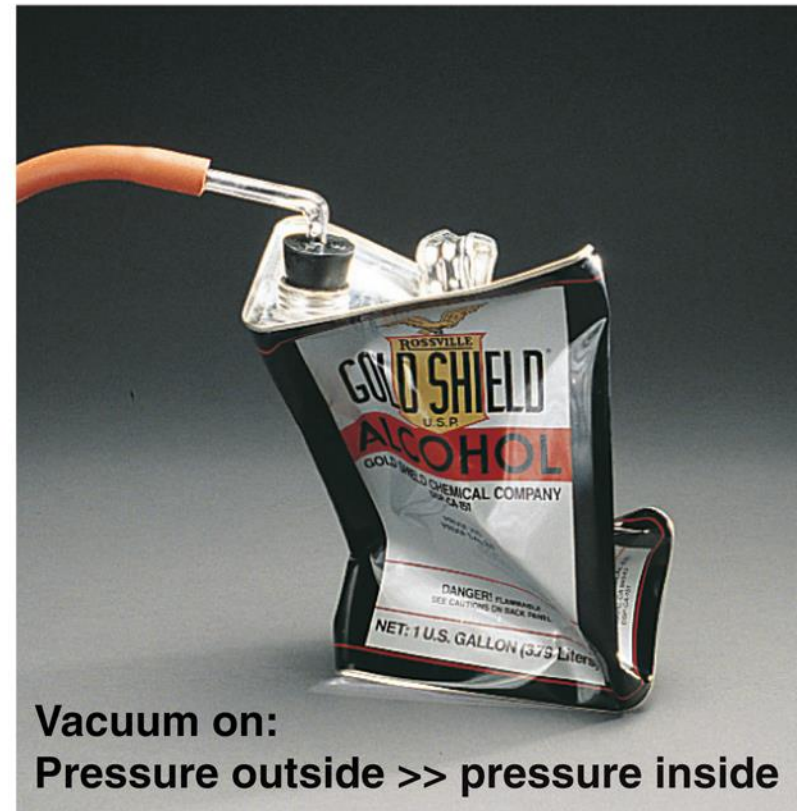
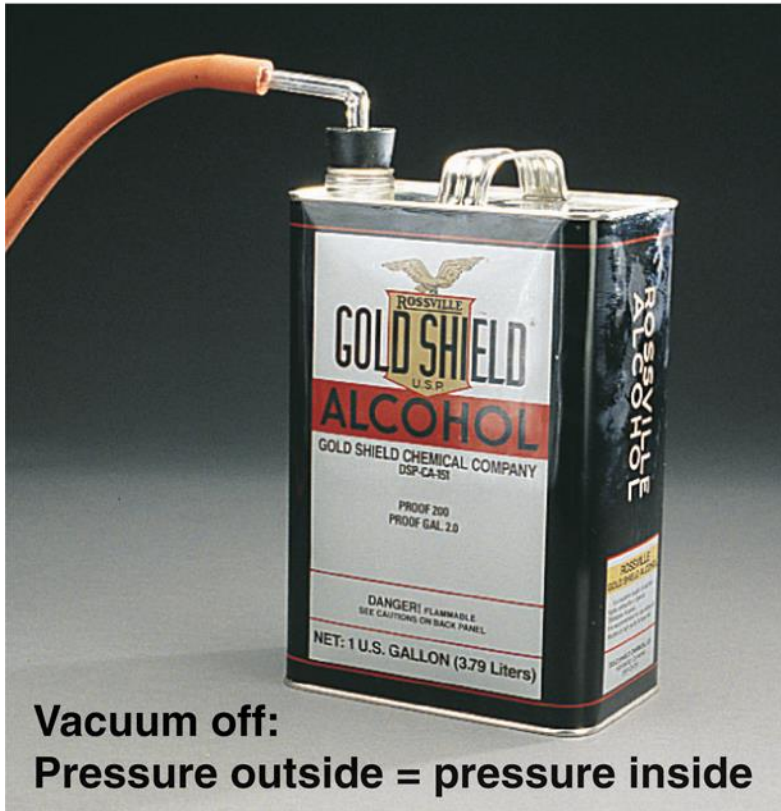
Atmospheric pressure arises from the force exerted by atmospheric gases on the earth's surface.

Atmospheric pressure decreases with altitude.



Figure 5.2 Effect of atmospheric pressure on a familiar object.

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Figure 5.3

A mercury barometer.

Invented by Evangelista Torricelli, Italian scientist, 1608-1647

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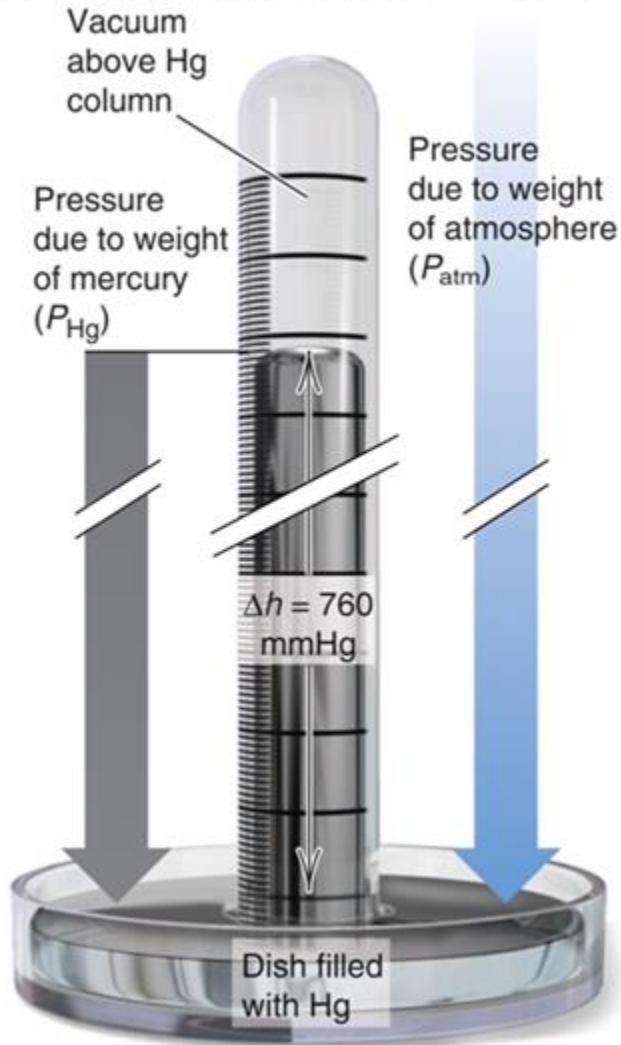


Figure 5.3a Water barometer.

Density of Hg × Height of Hg barometer = Density of water × Height of water barometer

$$\frac{\text{Density of Hg}}{\text{Density of water}} = \frac{\text{Height of water barometer}}{\text{Height of Hg barometer}}$$



Table 5.1 Common Units of Pressure

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Unit	Normal Atmospheric Pressure at Sea Level and 0°C
pascal (Pa); kilopascal (kPa)	1.01325×10^5 Pa; 101.325 kPa
atmosphere (atm)	1 atm*
millimeters of mercury (mmHg)	760 mmHg*
torr	760 torr*
pounds per square inch (lb/in ² or psi)	14.7 lb/in ²
bar	1.01325 bar

*This is an exact quantity; in calculations, we use as many significant figures as necessary.



Sample Problem 5.1

Converting Units of Pressure

PROBLEM: A geochemist heats a limestone (CaCO_3) sample and collects the CO_2 released in an evacuated flask attached to a closed-end manometer. After the system comes to room temperature, $\Delta h = 291.4$ mm Hg. Calculate the CO_2 pressure in torrs, atmospheres, and kilopascals.

PLAN: Construct conversion factors to find the other units of pressure.

$$\text{SOLUTION: } 291.4 \cancel{\text{ mmHg}} \times \frac{1 \text{ torr}}{1 \cancel{\text{ mmHg}}} = 291.4 \text{ torr}$$

$$291.4 \cancel{\text{ torr}} \times \frac{1 \text{ atm}}{760 \cancel{\text{ torr}}} = 0.3834 \text{ atm}$$

$$0.3834 \cancel{\text{ atm}} \times \frac{101.325 \text{ kPa}}{1 \cancel{\text{ atm}}} = 38.85 \text{ kPa}$$



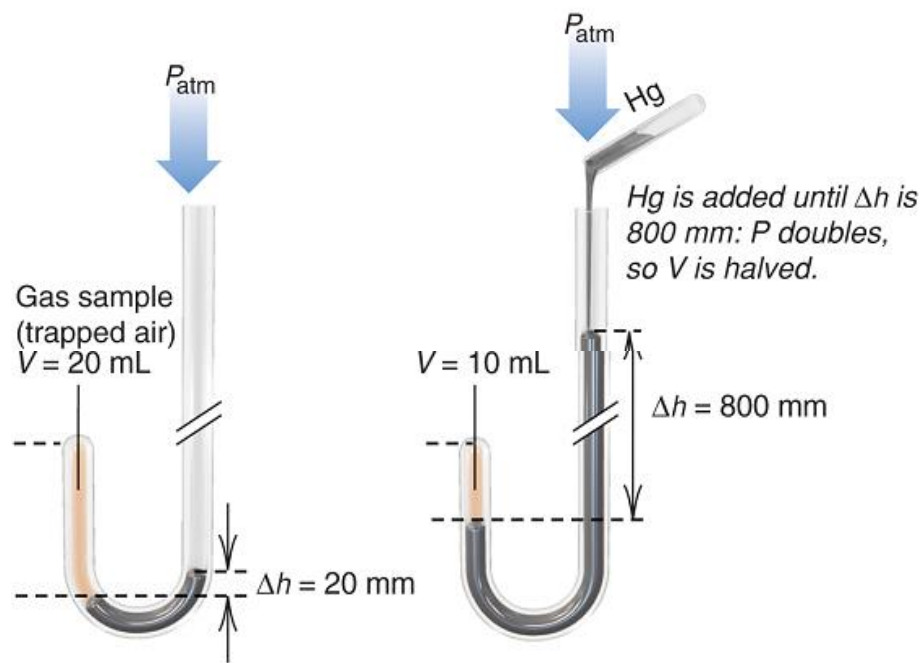
The Gas Laws

- The gas laws describe the physical behavior of gases in terms of 4 variables:
 - pressure (P)
 - temperature (T)
 - volume (V)
 - amount (number of moles, n)
- An ***ideal gas*** is a gas that exhibits linear relationships among these variables.
- ***No ideal gas actually exists***, but most simple gases behave nearly ideally at ordinary temperatures and pressures.



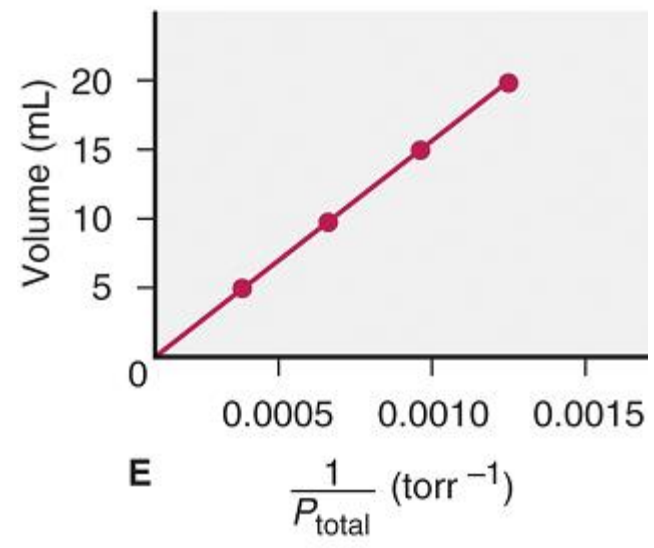
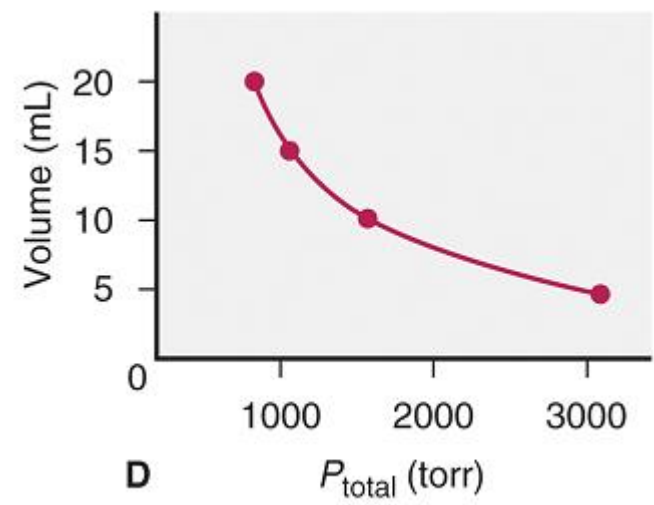
Figure 5.4 Boyle's law, the relationship between the volume and pressure of a gas.

Robert William Boyle was an Anglo-Irish (1627-1691)



A $P_{\text{total}} = P_{\text{atm}} + \Delta h$
 $= 760 \text{ torr} + 20 \text{ torr}$
 $= 780 \text{ torr}$

B $P_{\text{total}} = P_{\text{atm}} + \Delta h$
 $= 760 \text{ torr} + 800 \text{ torr}$
 $= 1560 \text{ torr}$



V (mL)	P (torr)			$\frac{1}{P_{\text{total}}}$	PV (torr·mL)
	Δh	$+ P_{\text{atm}}$	$= P_{\text{total}}$		
20.0	20.0	760	780	0.00128	1.56×10^4
15.0	278	760	1038	0.000963	1.56×10^4
10.0	800	760	1560	0.000641	1.56×10^4
5.0	2352	760	3112	0.000321	1.56×10^4

Boyle's Law

At constant temperature, the volume occupied by a fixed amount of gas is *inversely* proportional to the external pressure.

$$V \propto \frac{1}{P} \quad \text{or } PV = \text{constant}$$

At fixed T and n ,
 P decreases as V increases
 P increases as V decreases



Figure 5.5 AB

Charles's law, the relationship between the volume and temperature of a gas.

Jacques Alexandre César Charles was a French scientist, 1746-1823

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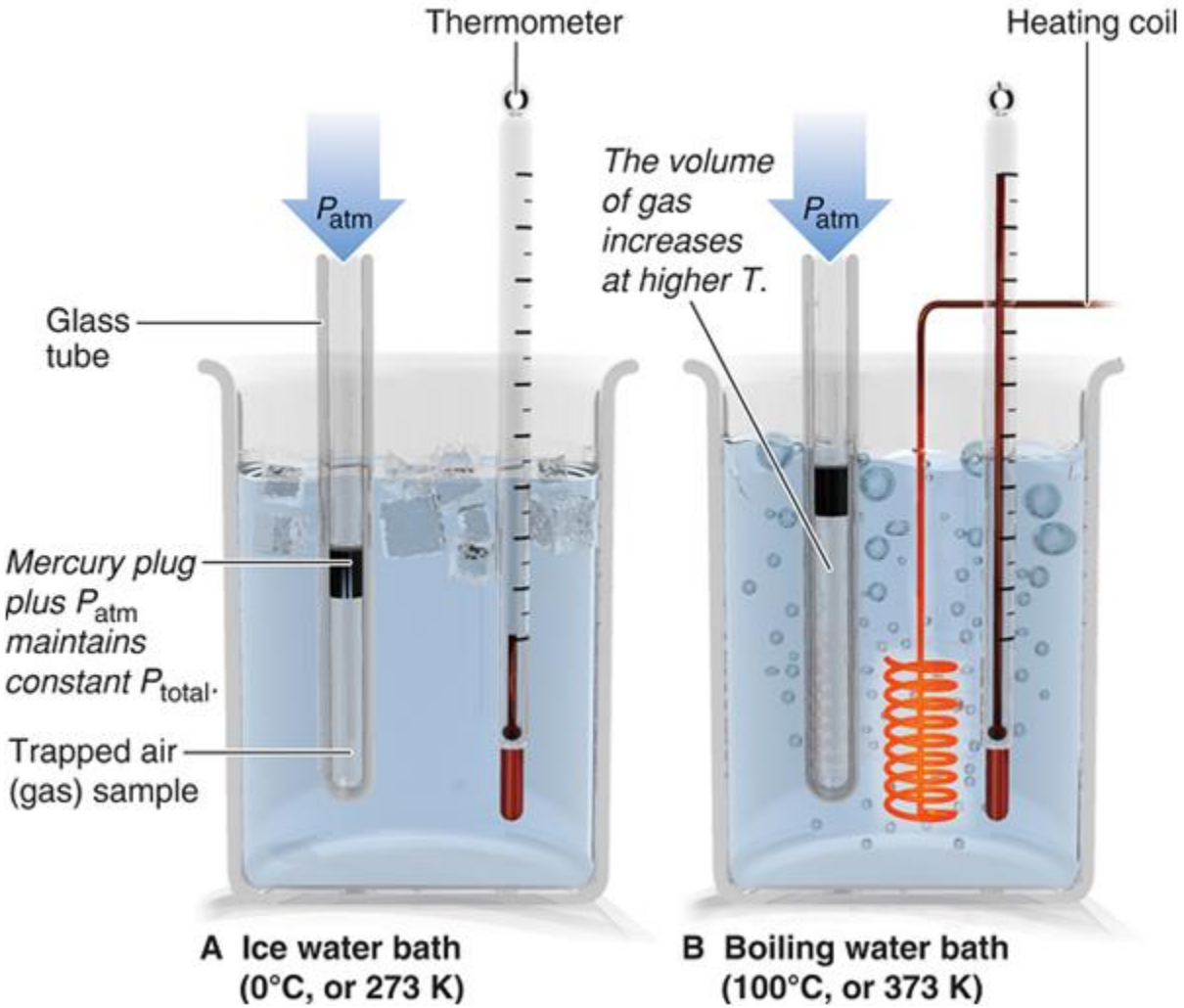
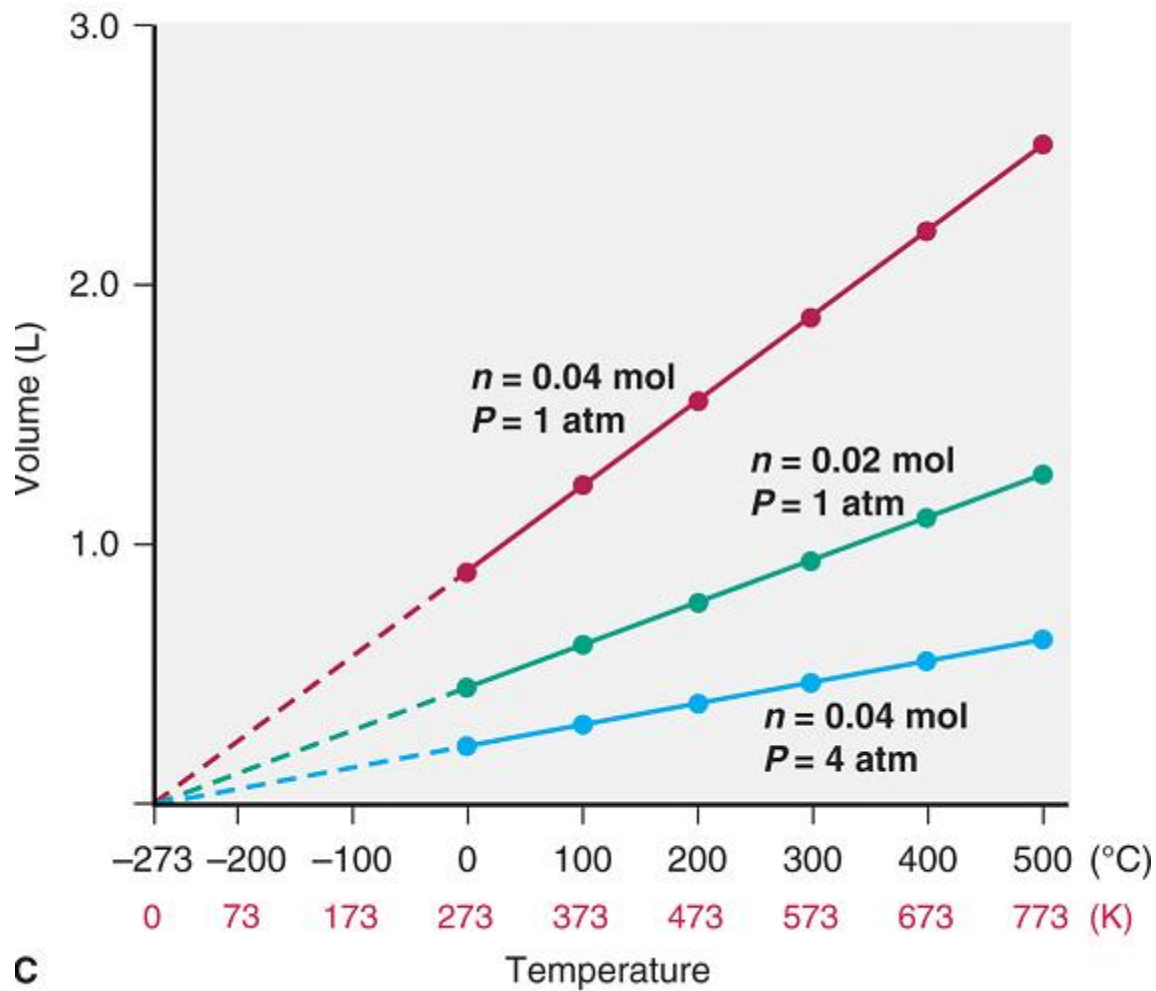


Figure 5.5 C

Absolute zero (0 K) is the temperature at which an ideal gas would have a zero volume.



c



Charles's Law

At constant pressure, the volume occupied by a fixed amount of gas is **directly** proportional to its absolute (Kelvin) temperature.

$$V \propto T \quad \frac{V}{T} = \text{constant}$$

At fixed P and n ,
 T decreases as V decreases
 T increases as V increases



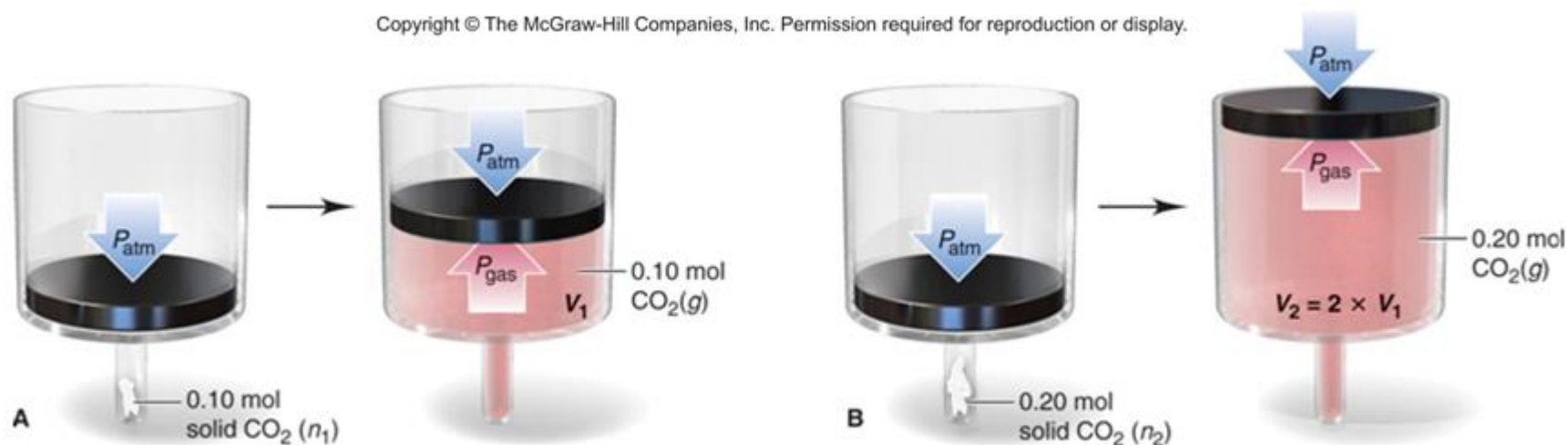
Figure 5.6

The relationship between the volume and amount of a gas.

Lorenzo Romano Amedeo Carlo Avogadro, was an Italian scientist, 1776-1856.

At fixed temperature and pressure, the volume occupied by a gas is directly proportional to the amount of gas.

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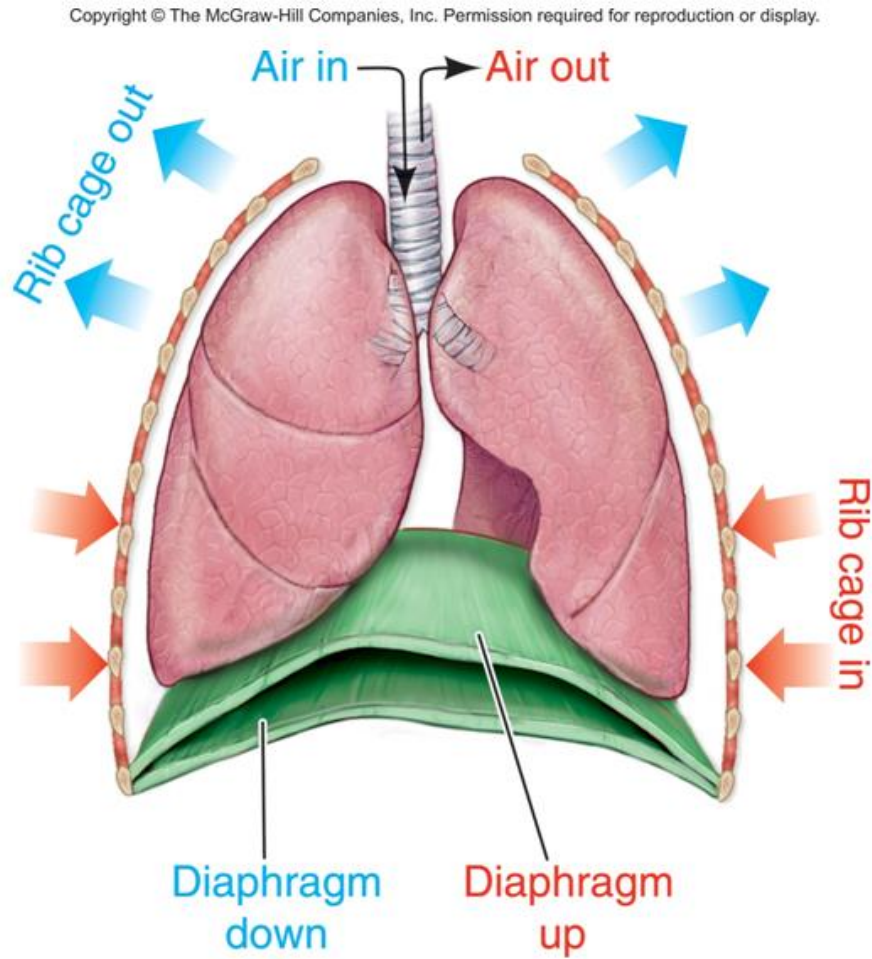


Avogadro's Law: at fixed temperature and pressure, equal volumes of *any* ideal gas contain equal numbers of particles (or moles).



Figure 5.7

The process of breathing applies the gas laws.



Gas Behavior at Standard Conditions

STP or **standard temperature and pressure** specifies a pressure of **1 atm (760 torr)** and a temperature of **0°C (273.15 K)**.

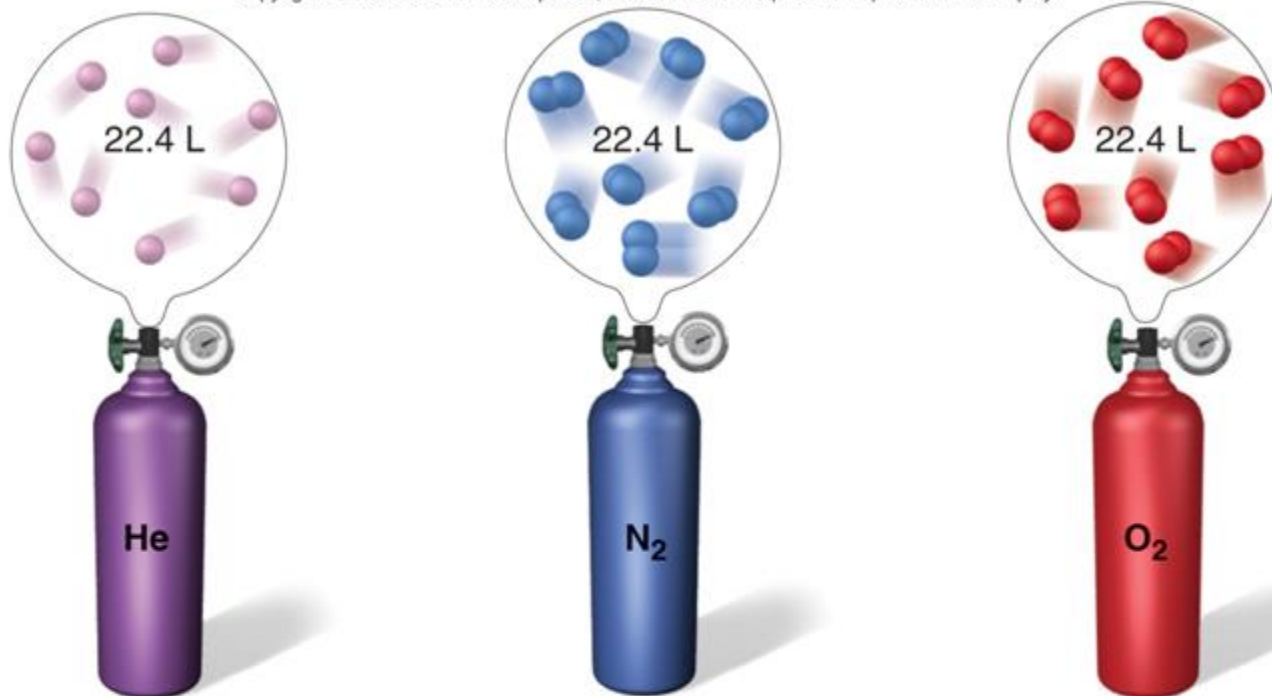
The **standard molar volume** is the volume of 1 mol of an ideal gas at STP.

Standard molar volume = 22.4141 L or **22.4 L**



Figure 5.8 Standard molar volume.

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$n = 1 \text{ mol}$	$n = 1 \text{ mol}$	$n = 1 \text{ mol}$
$P = 1 \text{ atm (760 torr)}$	$P = 1 \text{ atm (760 torr)}$	$P = 1 \text{ atm (760 torr)}$
$T = 0^\circ\text{C (273 K)}$	$T = 0^\circ\text{C (273 K)}$	$T = 0^\circ\text{C (273 K)}$
$V = 22.4 \text{ L}$	$V = 22.4 \text{ L}$	$V = 22.4 \text{ L}$
Number of gas particles $= 6.022 \times 10^{23}$	Number of gas particles $= 6.022 \times 10^{23}$	Number of gas particles $= 6.022 \times 10^{23}$
Mass = 4.003 g	Mass = 28.02 g	Mass = 32.00 g
$d = 0.179 \text{ g/L}$	$d = 1.25 \text{ g/L}$	$d = 1.43 \text{ g/L}$



The volume of 1 mol (22.4 L) of an ideal gas and of some familiar objects:

Figure 5.9



The Ideal Gas Law

$$pV = nRT$$

$$R = \frac{PV}{nT} = \frac{1 \text{ atm} \times 22.414 \text{ L}}{1 \text{ mol} \times 273.15 \text{ K}} = \frac{0.0821 \text{ atm}\cdot\text{L}}{\text{mol}\cdot\text{K}}$$

R is the universal gas constant;
the numerical value of R depends on the units used.

The ideal gas law can also be expressed by the combined equation:

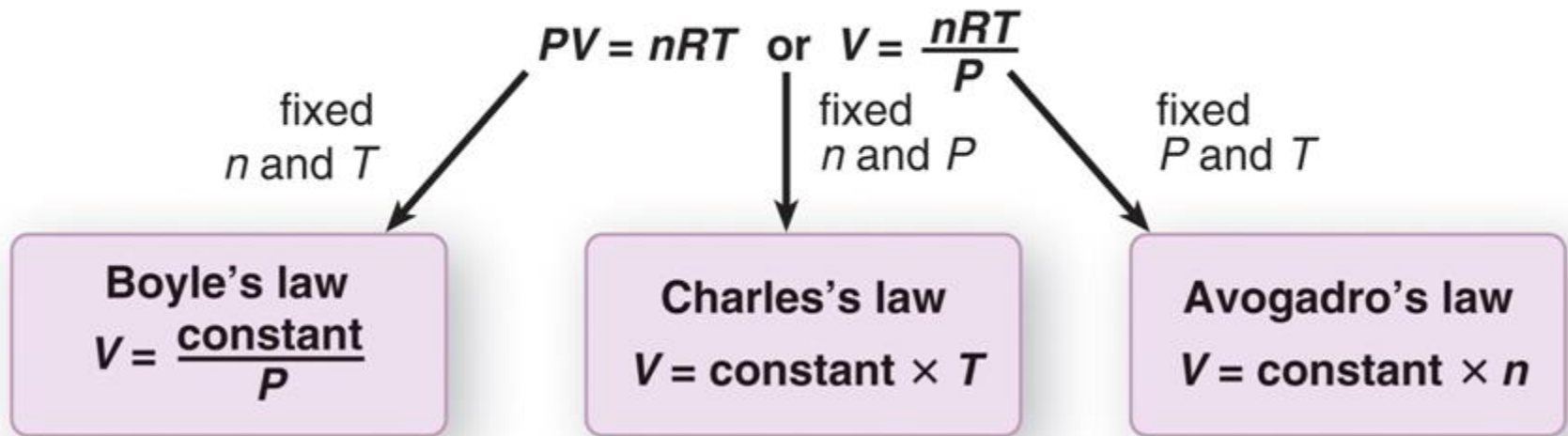
$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$



Figure 5.10 The individual gas laws as special cases of the ideal gas law.

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IDEAL GAS LAW

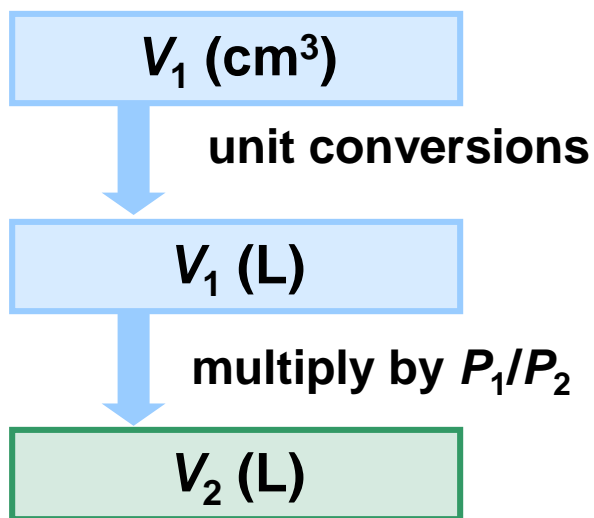


Sample Problem 5.2

Applying the Volume-Pressure Relationship

PROBLEM: Boyle's apprentice (تلميذ) finds that the air trapped in a J tube occupies 24.8 cm^3 at 1.12 atm . By adding mercury to the tube, he increases the pressure on the trapped air to 2.64 atm . Assuming constant temperature, what is the new volume of air (in L)?

PLAN: The temperature and amount of gas are fixed, so this problem involves a change in pressure and volume only.



Sample Problem 5.2

SOLUTION:

$$P_1 = 1.12 \text{ atm} \quad P_2 = 2.64 \text{ atm}$$

$$V_1 = 24.8 \text{ cm}^3 \quad V_2 = \text{unknown}$$

n and T are constant

$$24.8 \text{ cm}^3 \times \frac{1 \text{ mL}}{1 \text{ cm}^3} \times \frac{\text{L}}{10^3 \text{ mL}} = 0.0248 \text{ L}$$

$$\frac{P_1 V_1}{\cancel{n_1 T_1}} = \frac{P_2 V_2}{\cancel{n_2 T_2}}$$

$$P_1 V_1 = P_2 V_2$$

$$V_2 = V_1 \times \frac{P_1}{P_2} = 0.0248 \text{ L} \times \frac{1.12 \text{ atm}}{2.46 \text{ atm}} = \boxed{0.0105 \text{ L}}$$

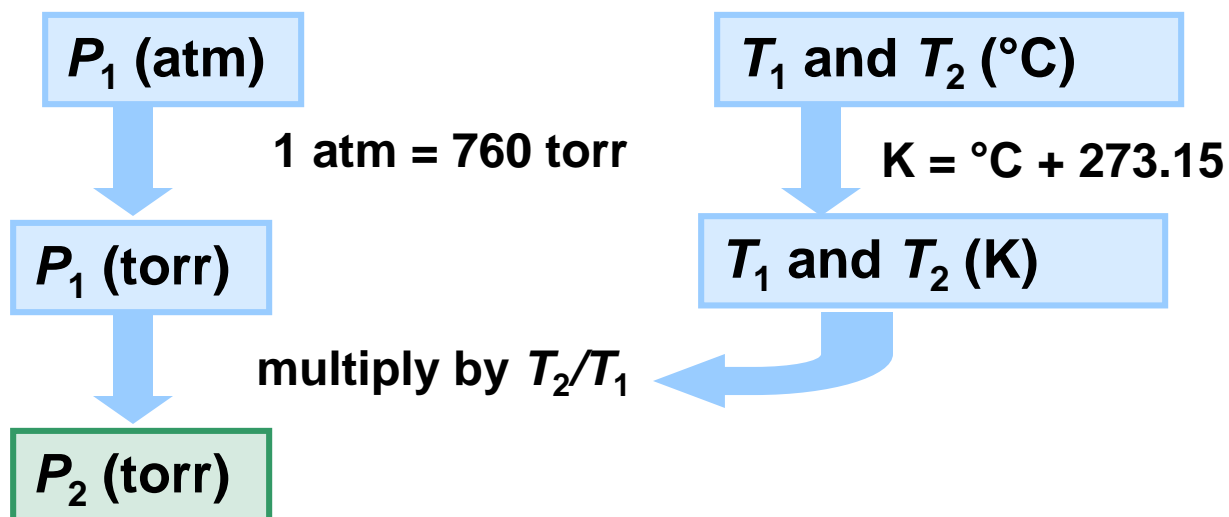


Sample Problem 5.3

Applying the Pressure-Temperature Relationship

PROBLEM: A steel tank used for fuel delivery is fitted with a safety valve that opens when the internal pressure exceeds 1.00×10^3 torr. It is filled with methane at 23°C and 0.991 atm and placed in boiling water at exactly 100°C . Will the safety valve open?

PLAN: We must determine if the pressure will exceed 1.00×10^3 torr at the new temperature. Since the gas is in a steel tank, the volume remains constant.



Sample Problem 5.3

SOLUTION:

$$P_1 = 0.991 \text{ atm} \quad P_2 = \text{unknown}$$

$$T_1 = 23^\circ\text{C} \quad T_2 = 100.^\circ\text{C}$$

n and V are constant

$$0.991 \text{ atm} \times \frac{760 \text{ torr}}{1 \text{ atm}} = 753 \text{ torr}$$

$$T_1 = 23 + 273.15 = 296 \text{ K}$$

$$T_2 = 100. + 273.15 = 373 \text{ K}$$

$$\frac{P_1 \cancel{V_1}}{\cancel{n_1} T_1} = \frac{P_2 \cancel{V_2}}{\cancel{n_2} T_2}$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$P_2 = P_1 \times \frac{T_2}{T_1} = 753 \text{ torr} \times \frac{373 \text{ K}}{296 \text{ K}} = \boxed{949 \text{ torr}}$$

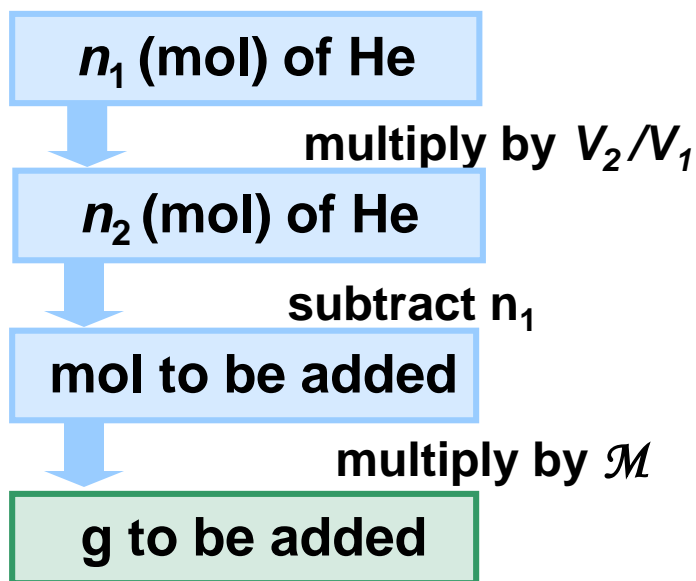
The safety valve will not open, since P_2 is less than 1.00×10^3 torr.



Sample Problem 5.4 Applying the Volume-Amount Relationship

PROBLEM: A scale model of a blimp rises when it is filled with helium to a volume of 55.0 dm^3 . When 1.10 mol of He is added to the blimp, the volume is 26.2 dm^3 . How many more grams of He must be added to make it rise? Assume constant T and P .

PLAN: The initial amount of helium (n_1) is given, as well as the initial volume (V_1) and the volume needed to make it rise (V_2). We need to calculate n_2 and hence the mass of He to be added.



Sample Problem 5.4

SOLUTION:

$$n_1 = 1.10 \text{ mol}$$

$$n_2 = \text{unknown}$$

$$V_1 = 26.2 \text{ dm}^3$$

$$V_2 = 55.0 \text{ dm}^3$$

T and P are constant

$$\frac{\cancel{P}_1 V_1}{n_1 \cancel{T}_1} = \frac{\cancel{P}_2 V_2}{n_2 \cancel{T}_2}$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$n_2 = n_1 \times \frac{V_2}{V_1} = 1.10 \text{ mol} \times \frac{55.0 \text{ dm}^3}{26.2 \text{ dm}^3} = 2.31 \text{ mol He}$$

Additional amount of He needed = $2.31 \text{ mol} - 1.10 \text{ mol} = 1.21 \text{ mol He}$

$$1.21 \text{ mol He} \times \frac{4.003 \text{ g He}}{1 \text{ mol He}} = \boxed{4.84 \text{ g He}}$$



Sample Problem 5.5

Solving for an Unknown Gas Variable at Fixed Conditions

PROBLEM: A steel tank has a volume of 438 L and is filled with 0.885 kg of O₂. Calculate the pressure of O₂ at 21°C.

PLAN: We are given V , T and mass, which can be converted to moles (n). Use the ideal gas law to find P .

SOLUTION: $V = 438 \text{ L}$ $T = 21^\circ\text{C} = 294 \text{ K}$
 $n = 0.885 \text{ kg O}_2$ (convert to mol) P is unknown

$$0.885 \text{ kg O}_2 \times \frac{10^3 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2} = 27.7 \text{ mol O}_2$$

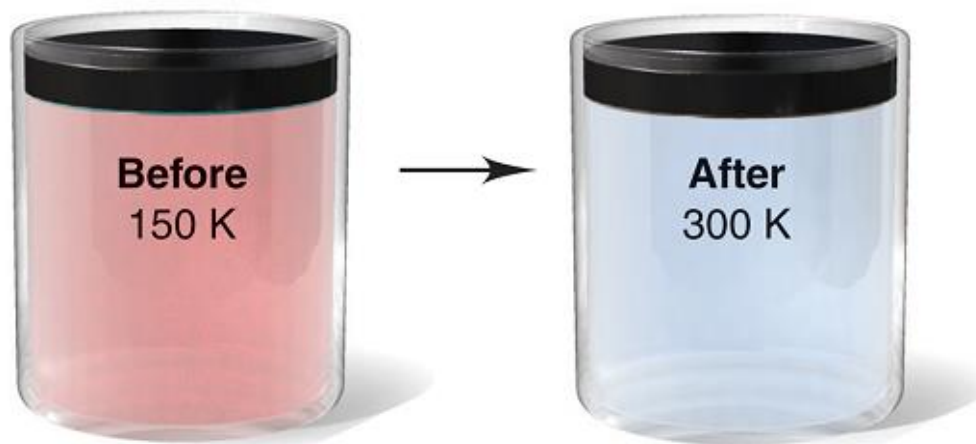
$$P = \frac{nRT}{V} = \frac{27.7 \text{ mol} \times 0.0821 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 294.15 \text{ K}}{438 \text{ L}} = 1.53 \text{ atm}$$



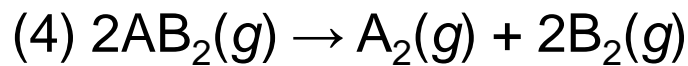
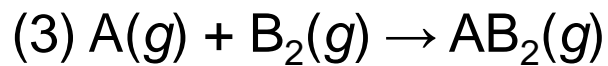
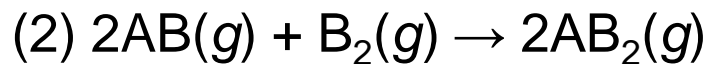
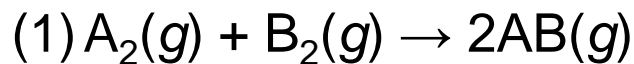
Sample Problem 5.6

Using Gas Laws to Determine a Balanced Equation

PROBLEM: The piston-cylinder is depicted before and after a gaseous reaction that is carried out at constant pressure. The temperature is 150 K before the reaction and 300 K after the reaction. (Assume the cylinder is insulated.)



Which of the following balanced equations describes the reaction?

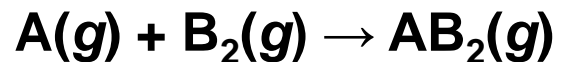


Sample Problem 5.6

PLAN: We are told that P is constant for this system, and the depiction shows that V does not change either. Since T changes, the volume could not remain the same unless the amount of gas in the system also changes.

SOLUTION: $n_1 T_1 = n_2 T_2 \quad \frac{n_2}{n_1} = \frac{T_1}{T_2} = \frac{150 \text{ K}}{300 \text{ K}} = \frac{1}{2}$

Since T doubles, the total number of moles of gas must halve – i.e., the moles of product must be half the moles of reactant. This relationship is shown by equation (3).



The Ideal Gas Law and Gas Density

The density of a gas is

- directly proportional to its molar mass and
- inversely proportional to its temperature.

$$\text{density} = \frac{m}{V} \quad \text{and} \quad \text{moles} = \frac{m}{\mathcal{M}}$$

$$PV = \frac{m}{\mathcal{M}} RT$$

$$\frac{m}{V} = d = \frac{\mathcal{M} \times P}{RT}$$



Sample Problem 5.7

Calculating Gas Density

PROBLEM: Find the density (in g/L) of $\text{CO}_2(g)$ and the number of molecules per liter

(a) at STP and (b) at room conditions ($20.^\circ\text{C}$ and 1.00 atm).

PLAN: We can use the molar mass of CO_2 to find its density from the ideal gas equation.

SOLUTION: (a) At STP, or 273 K and 1.00 atm :

$$d = \frac{M \times P}{RT} = \frac{44.01 \text{ g/mol} \times 1.00 \text{ atm}}{0.0821 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 273 \text{ K}} = 1.96 \text{ g/L}$$

$$\frac{1.96 \text{ g CO}_2}{1 \text{ L}} \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol}}$$

$$= 2.68 \times 10^{22} \text{ molecules CO}_2/\text{L}$$



Sample Problem 5.7

SOLUTION: (b) At 20.°C and 1.00 atm:

$$T = 20.^\circ\text{C} + 273.15 = 293 \text{ K}$$

$$d = \frac{M \times P}{RT} = \frac{44.01 \text{ g/mol} \times 1.00 \text{ atm}}{0.0821 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 293 \text{ K}} = 1.83 \text{ g/L}$$

$$\frac{1.83 \text{ g CO}_2}{1 \text{ L}} \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol}}$$

$$= 2.50 \times 10^{22} \text{ molecules CO}_2/\text{L}$$



Molar Mass from the Ideal Gas Law

$$n = \frac{m}{\mathcal{M}} = \frac{PV}{RT}$$

$$\mathcal{M} = \frac{mRT}{PV}$$



Sample Problem 5.8

Finding the Molar Mass of a Volatile Liquid

PROBLEM: An organic chemist isolates a colorless liquid from a petroleum sample. She places the liquid in a preweighed flask and puts the flask in boiling water, causing the liquid to vaporize and fill the flask with gas. She closes the flask and reweighs it. She obtains the following data:

Volume (V) of flask = 213 mL
mass of flask + gas = 78.416 g

$T = 100.0^{\circ}\text{C}$ $P = 754$ torr
mass of flask = 77.834 g

Calculate the molar mass of the liquid.

PLAN: The variables V , T and P are given. We find the mass of the gas by subtracting the mass of the flask from the mass of the flask with the gas in it, and use this information to calculate M .



Sample Problem 5.8

SOLUTION: m of gas = $(78.416 - 77.834) = 0.582$ g

$$V = 213 \text{ mL} \times \frac{1 \text{ L}}{10^3 \text{ mL}} = 0.213 \text{ L} \quad T = 100.0^\circ\text{C} + 273.15 = 373.2 \text{ K}$$

$$P = 754 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.992 \text{ atm}$$

$$\mathcal{M} = \frac{mRT}{PV} = \frac{0.582 \text{ g} \times 0.0821 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 373 \text{ K}}{0.213 \text{ L} \times 0.992 \text{ atm}}$$

$$= 84.4 \text{ g/mol}$$



Mixtures of Gases

- Gases mix homogeneously in any proportions.
 - Each gas in a mixture behaves as if it were the only gas present.
- The pressure exerted by each gas in a mixture is called its ***partial pressure***.
- Dalton's Law of partial pressures states that the total pressure in a mixture is the sum of the partial pressures of the component gases.
- The partial pressure of a gas is proportional to its mole fraction:

$$P_A = X_A \times P_{\text{total}}$$

$$X_A = \frac{n_A}{n_{\text{total}}}$$

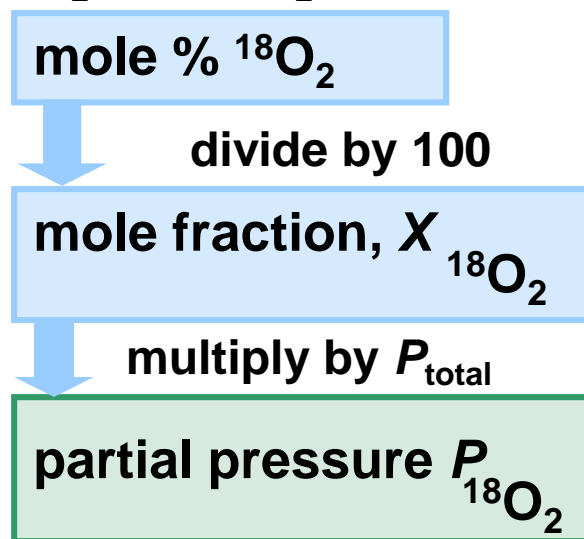


Sample Problem 5.9

Applying Dalton's Law of Partial Pressures

PROBLEM: In a study of O_2 uptake by muscle at high altitude, a physiologist prepares an atmosphere consisting of 79 mole N_2 , 17 mole $^{16}O_2$, and 4.0 mole $^{18}O_2$. (The isotope ^{18}O will be measured to determine the O_2 uptake.) The pressure of the mixture is 0.75 atm to simulate high altitude. Calculate the mole fraction and partial pressure of $^{18}O_2$ in the mixture.

PLAN: Find $X_{^{18}O_2}$ and $P_{^{18}O_2}$ from P_{total} and mol % $^{18}O_2$.



Sample Problem 5.9

SOLUTION:

$$X_{^{18}\text{O}_2} = \frac{4.0 \text{ mol } ^{18}\text{O}_2}{100} = 0.040$$

$$P_{^{18}\text{O}_2} = X_{^{18}\text{O}_2} \times P_{\text{total}} = 0.040 \times 0.75 \text{ atm} = \mathbf{0.030 \text{ atm}}$$

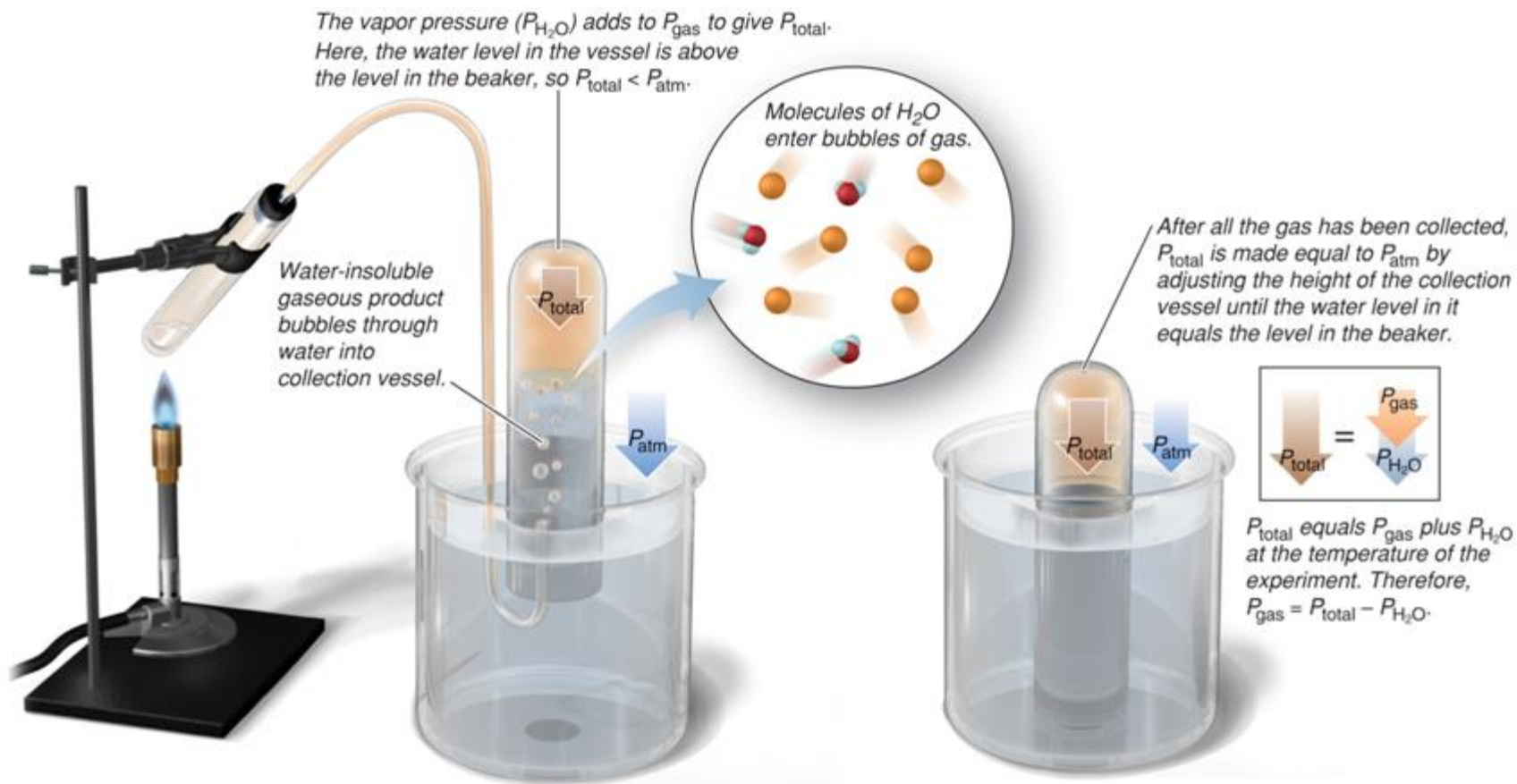


Table 5.2 Vapor Pressure of Water ($P_{\text{H}_2\text{O}}$) + at Different T

$T(^{\circ}\text{C})$	$P_{\text{H}_2\text{O}}$ (torr)	$T(^{\circ}\text{C})$	$P_{\text{H}_2\text{O}}$ (torr)
0	4.6	40	55.3
5	6.5	45	71.9
10	9.2	50	92.5
12	10.5	55	118.0
14	12.0	60	149.4
16	13.6	65	187.5
18	15.5	70	233.7
20	17.5	75	289.1
22	19.8	80	355.1
24	22.4	85	433.6
26	25.2	90	525.8
28	28.3	95	633.9
30	31.8	100	760.0
35	42.2		



Figure 5.11 Collecting a water-insoluble gaseous product and determining its pressure.



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Sample Problem 5.10

Calculating the Amount of Gas Collected over Water

PROBLEM: Acetylene (C_2H_2) is produced in the laboratory when calcium carbide (CaC_2) reacts with water:



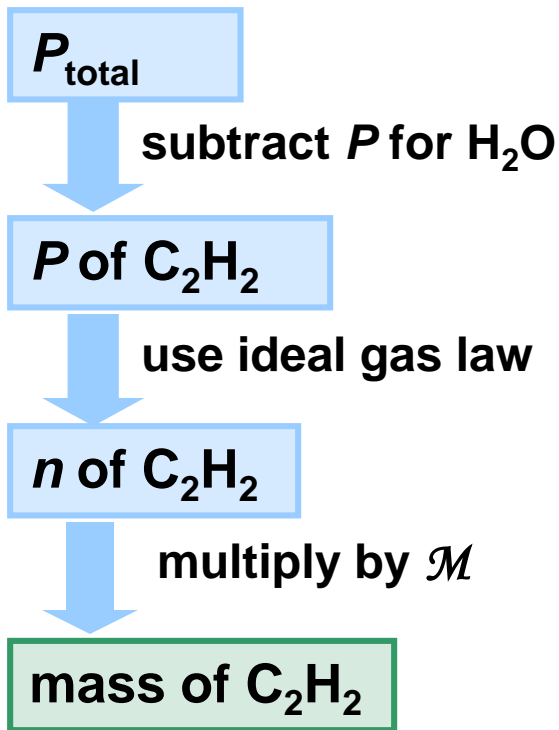
A collected sample of acetylene has a total gas pressure of 738 torr and a volume of 523 mL. At the temperature of the gas (23°C), the vapor pressure of water is 21 torr. How many grams of acetylene are collected?

PLAN: The difference in pressures will give P for the C_2H_2 . The number of moles (n) is calculated from the ideal gas law and converted to mass using the molar mass.



Sample Problem 5.10

PLAN:



SOLUTION:

$$P_{\text{C}_2\text{H}_2} = (738 - 21) \text{ torr} = 717 \text{ torr}$$

$$P = 717 \text{ ~~torr~~} \times \frac{1 \text{ atm}}{760 \text{ ~~torr~~}} = 0.943 \text{ atm}$$

$$V = 523 \text{ ~~mL~~} \times \frac{1 \text{ L}}{10^3 \text{ ~~mL~~}} = 0.523 \text{ L}$$

$$T = 23^\circ\text{C} + 273.15 \text{ K} = 296 \text{ K}$$



Sample Problem 5.10

SOLUTION:

$$n_{\text{C}_2\text{H}_2} = \frac{PV}{RT} = \frac{0.943 \text{ atm} \times 0.523 \text{ L}}{0.0821 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 296 \text{ K}} = 0.0203 \text{ mol}$$

$$0.0203 \text{ mol} \times \frac{26.04 \text{ g C}_2\text{H}_2}{1 \text{ mol C}_2\text{H}_2} = 0.529 \text{ g C}_2\text{H}_2$$



The Ideal Gas Law and Stoichiometry

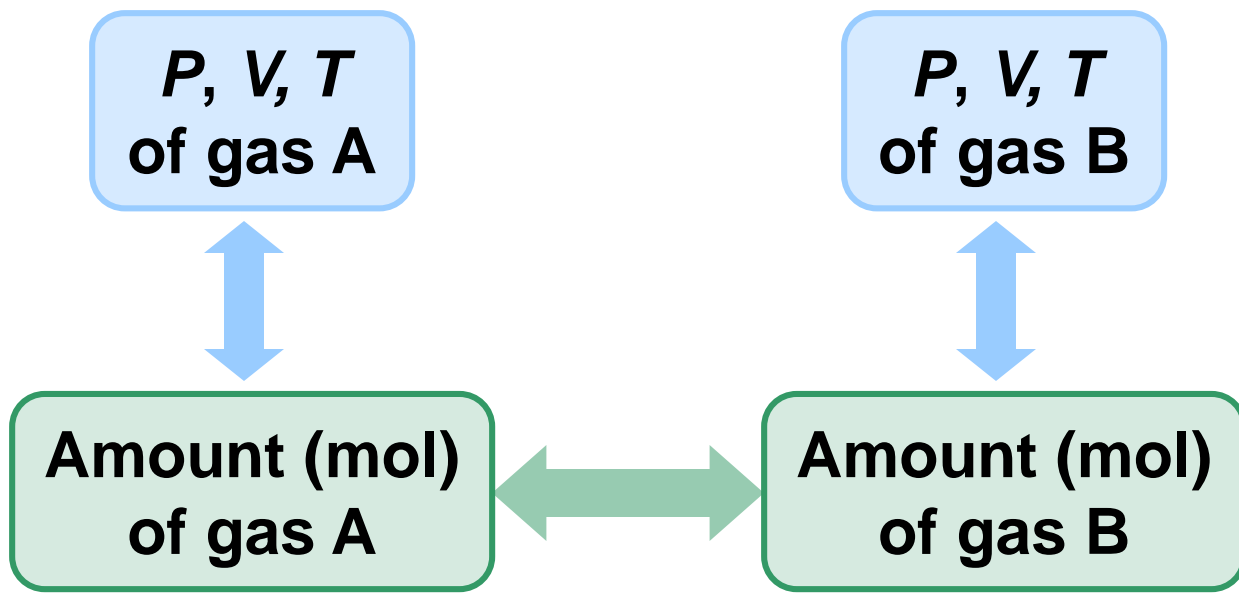


Figure 15.12

The relationships among the amount (mol, n) of gaseous reactant (or product) and the gas pressure (P), volume (V), and temperature (T).

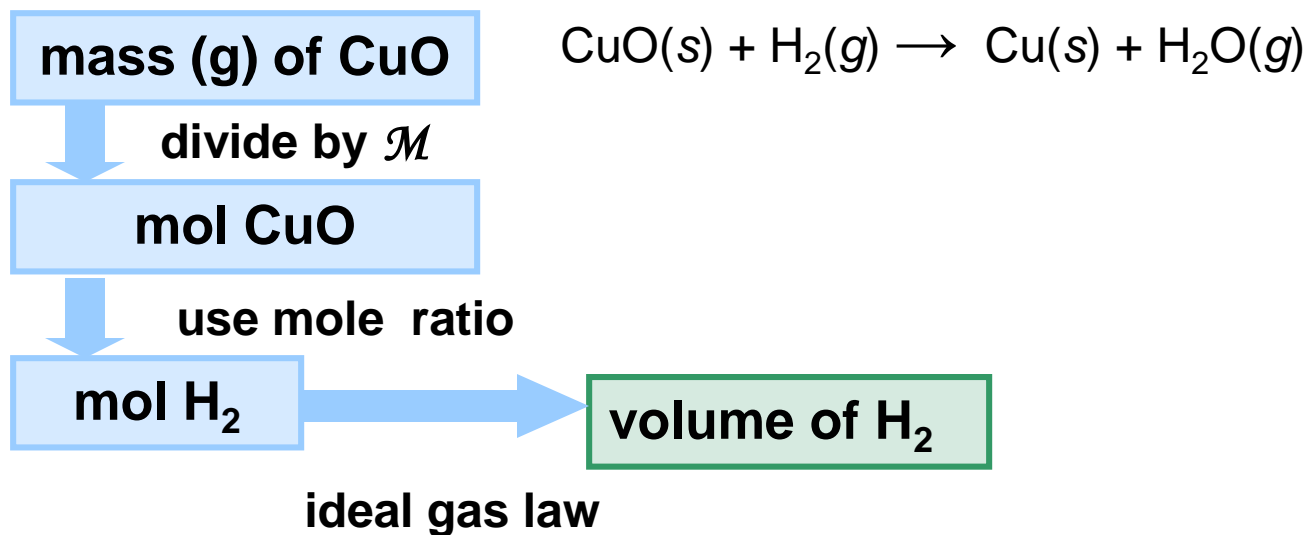


Sample Problem 5.11

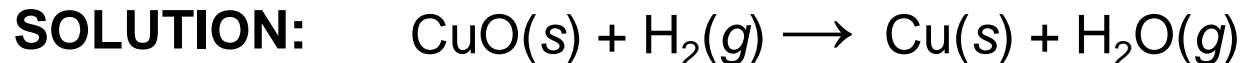
Using Gas Variables to Find Amounts of Reactants and Products I

PROBLEM: What volume of H_2 gas at 765 torr and 225°C is needed to reduce 35.5 g of copper(II) oxide to form pure copper and water?

PLAN: Write a balanced equation. Convert the mass of copper (II) oxide to moles and find the moles of H_2 , using the mole ratio from the balanced equation. Calculate the corresponding volume of H_2 using the ideal gas law.



Sample Problem 5.11



$$35.5 \text{ g CuO} \times \frac{1 \text{ mol CuO}}{79.55 \text{ g CuO}} \times \frac{1 \text{ mol H}_2}{1 \text{ mol CuO}} = 0.446 \text{ mol H}_2$$

$$P = 765 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 1.01 \text{ atm} \quad T = 225^\circ\text{C} + 273.15 \text{ K} = 498 \text{ K}$$

$$V = \frac{nRT}{P} = \frac{0.446 \text{ mol H}_2 \times 0.0821 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 498 \text{ K}}{1.01 \text{ atm}} = 18.1 \text{ L H}_2$$



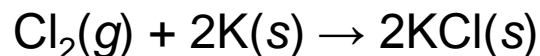
Sample Problem 5.12

Using Gas Variables to Find Amounts of Reactants and Products II

PROBLEM: What mass of potassium chloride forms when 5.25 L of chlorine gas at 0.950 atm and 293 K reacts with 17.0 g of potassium metal?

PLAN: First we must write a balanced equation. Since the quantities of both reactants are given, we must next determine which reactant is limiting. We will use the ideal gas law to calculate the moles of Cl_2 present.

SOLUTION: The balanced equation is:



For Cl_2 :

$P = 0.950 \text{ atm}$ $V = 5.25 \text{ L}$

$T = 293 \text{ K}$ $n = \text{unknown}$



Sample Problem 5.12

$$n_{\text{Cl}_2} = \frac{PV}{RT} = \frac{0.950 \text{ atm} \times 5.25 \text{ L}}{0.0821 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 293 \text{ K}} = 0.207 \text{ mol Cl}_2$$

$$\text{For Cl}_2: \quad 0.207 \text{ mol Cl}_2 \times \frac{2 \text{ mol KCl}}{1 \text{ mol Cl}_2} = 0.414 \text{ mol KCl}$$

$$\text{For K:} \quad 17.0 \text{ g K} \times \frac{1 \text{ mol K}}{39.10 \text{ g K}} \times \frac{2 \text{ mol KCl}}{2 \text{ mol K}} = 0.435 \text{ mol KCl}$$

Cl₂ is the limiting reactant.

$$0.414 \text{ mol KCl} \times \frac{74.55 \text{ g KCl}}{1 \text{ mol KCl}} = \boxed{30.9 \text{ g KCl}}$$



The Kinetic-Molecular Theory: A Model for Gas Behavior

Postulate 1:

Gas particles are tiny with large spaces between them. The volume of each particle is so small compared to the total volume of the gas that it is assumed to be zero.

Postulate 2:

Gas particles are in constant, random, straight-line motion except when they collide with each other or with the container walls.

Postulate 3:

Collisions are elastic, meaning that colliding particles exchange energy but do not lose any energy due to friction. Their *total kinetic energy is constant*. Between collisions the particles do not influence each other by attractive or repulsive forces.



Figure 5.13 Distribution of molecular speeds for N_2 at three temperatures.

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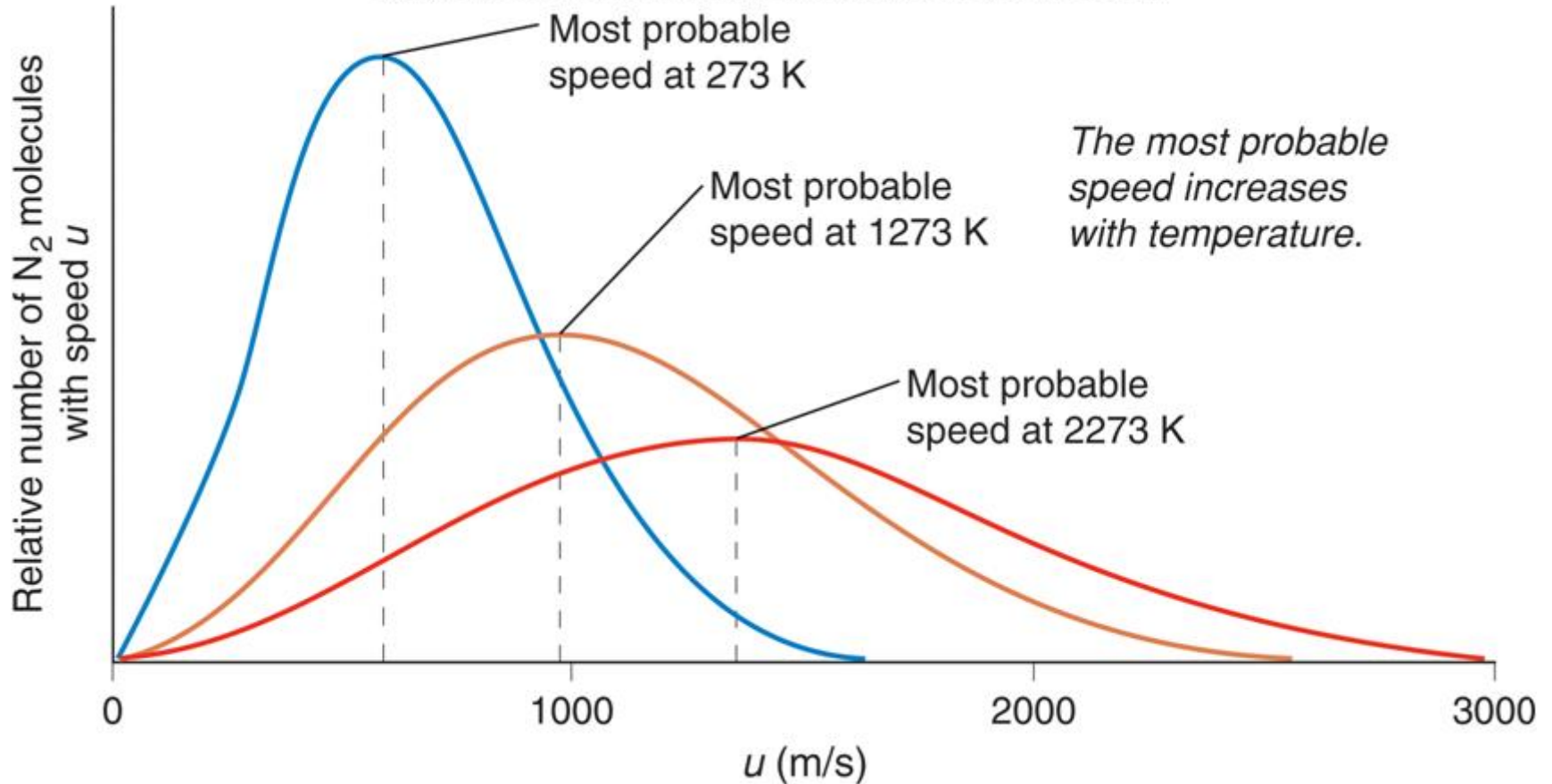


Figure 5.14 Pressure arises from countless collisions between gas particles and walls.

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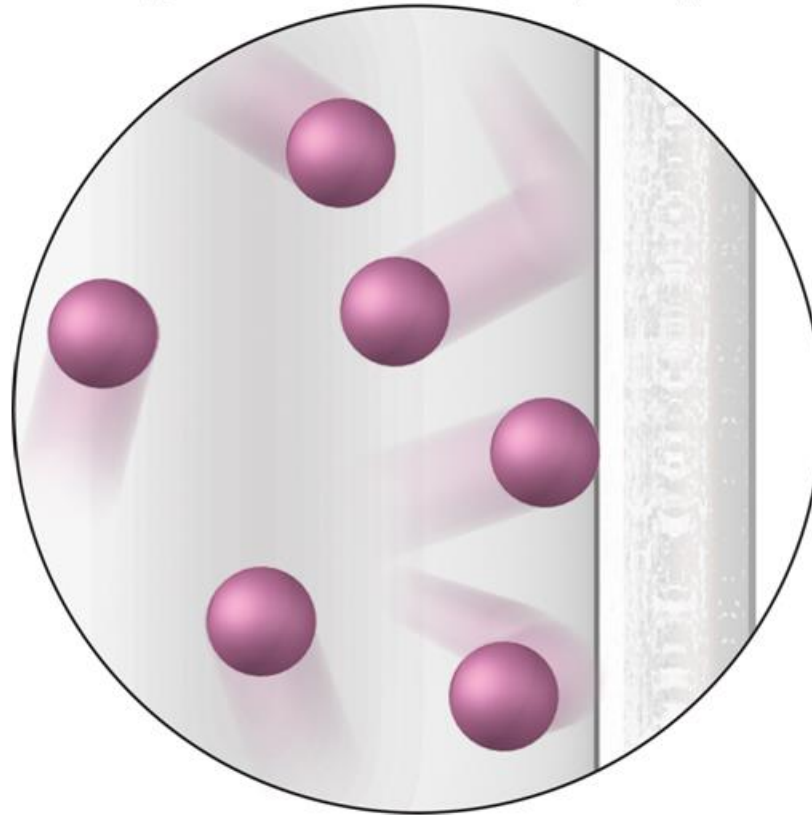
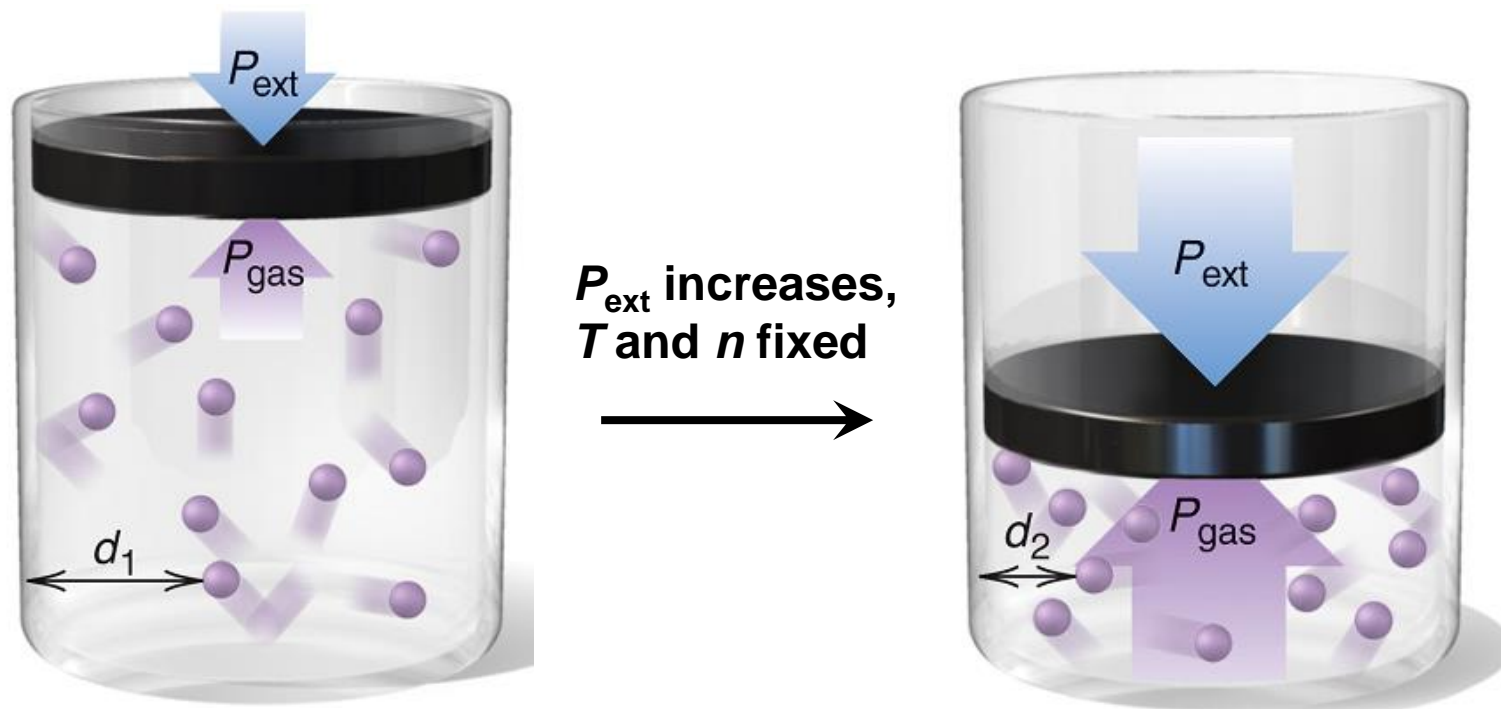


Figure 5.15 A molecular view of Boyle's law.

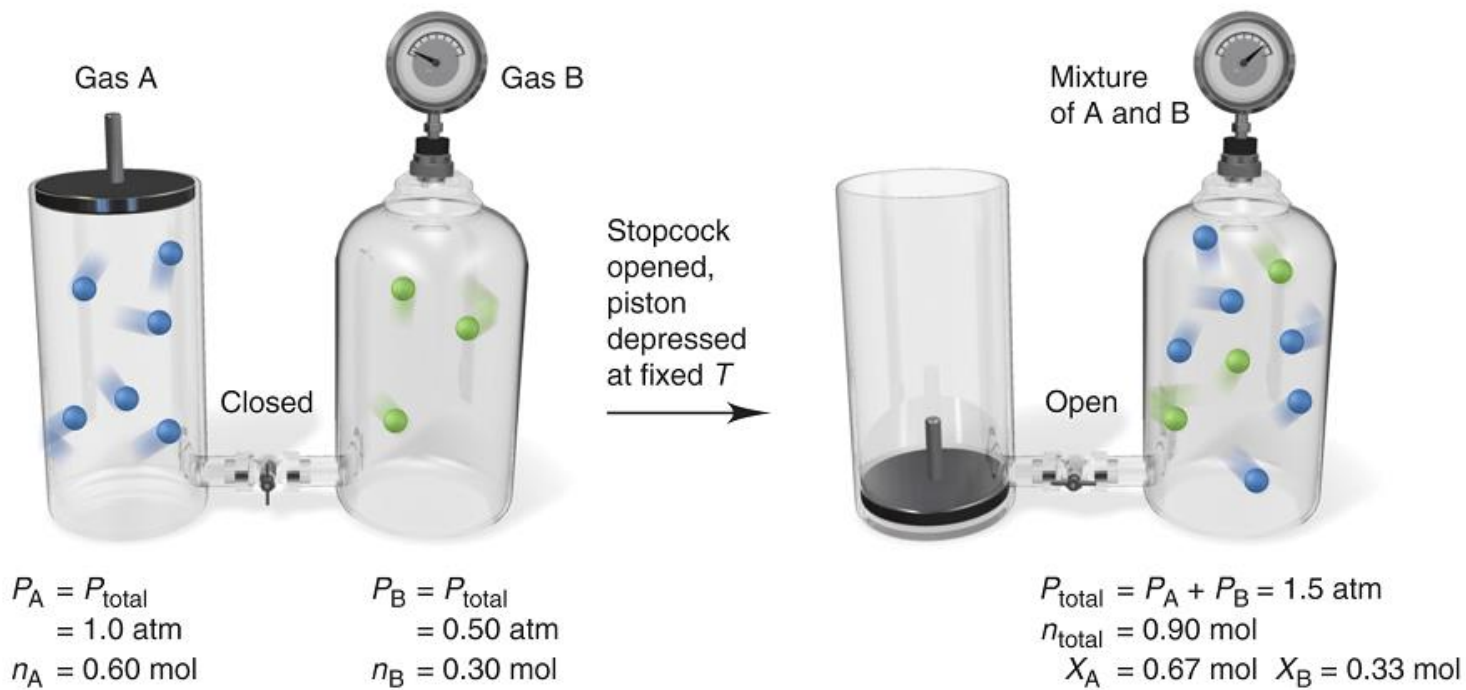


At any T , $P_{\text{gas}} = P_{\text{ext}}$ as particles hit the walls from an average distance, d_1 .

Higher P_{ext} causes lower V , which results in more collisions, because particles hit the walls from a shorter average distance ($d_2 < d_1$). As a result, $P_{\text{gas}} = P_{\text{ext}}$ again.



Figure 5.16 A molecular view of Dalton's law

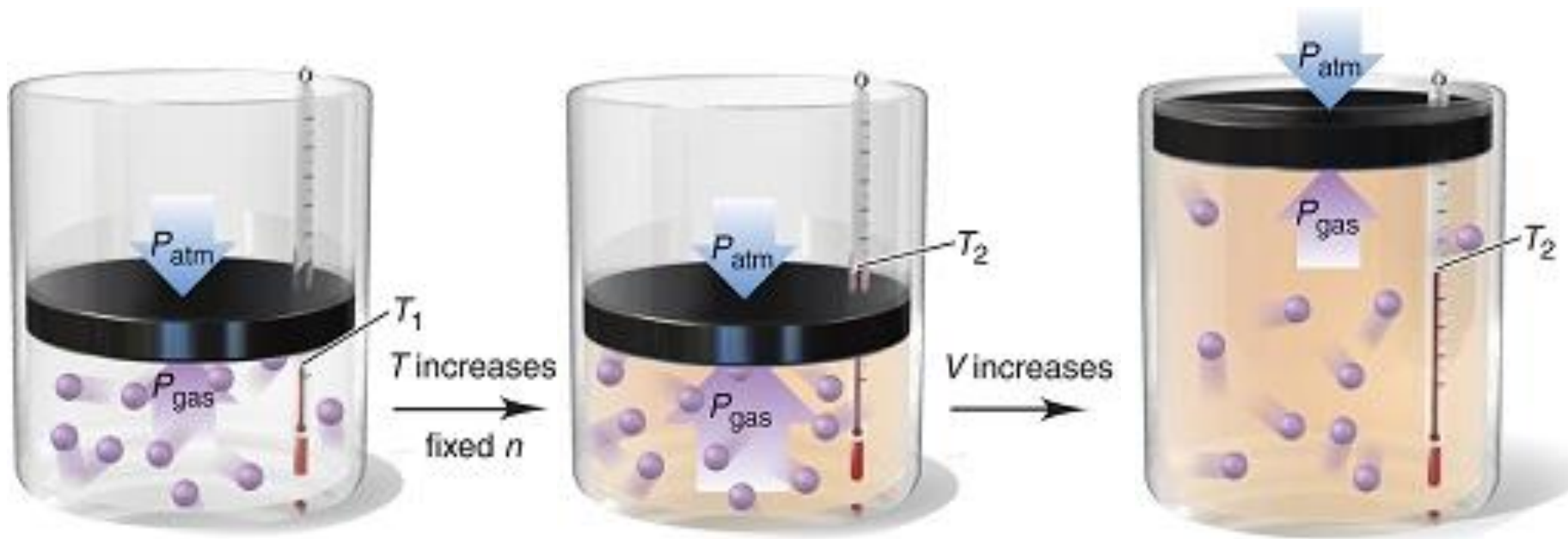


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Figure 5.17

A molecular view of Charles's law



At T_1 , $P_{gas} = P_{atm}$.

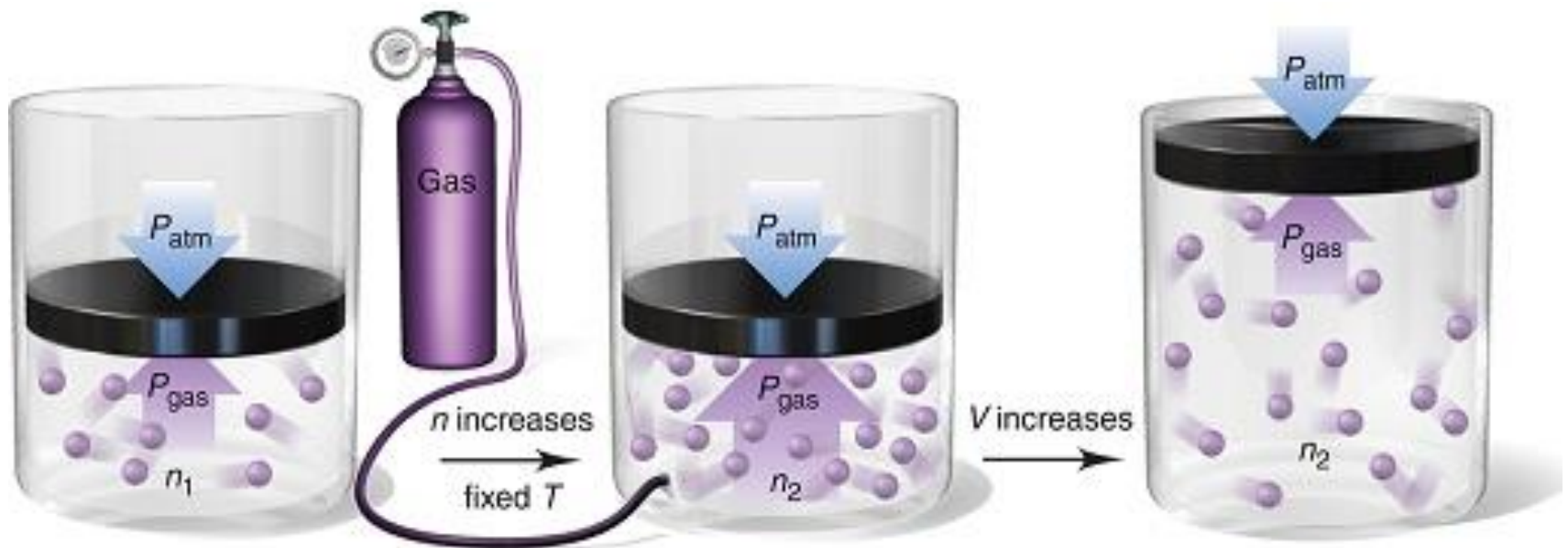
Higher T increases collision frequency, so $P_{gas} > P_{atm}$.

Thus, V increases until $P_{gas} = P_{atm}$ at T_2 .



Figure 5.18

A molecular view of Avogadro's law



For a given amount, n_1 , of gas, $P_{gas} = P_{atm}$.

When gas is added to reach n_2 the collision frequency of the particles increases, so $P_{gas} > P_{atm}$.

As a result, V increases until $P_{gas} = P_{atm}$ again.



Kinetic Energy and Gas Behavior

At a given T , all gases in a sample have the same average kinetic energy.

$$E_k = \frac{1}{2} \text{ mass x speed}^2$$

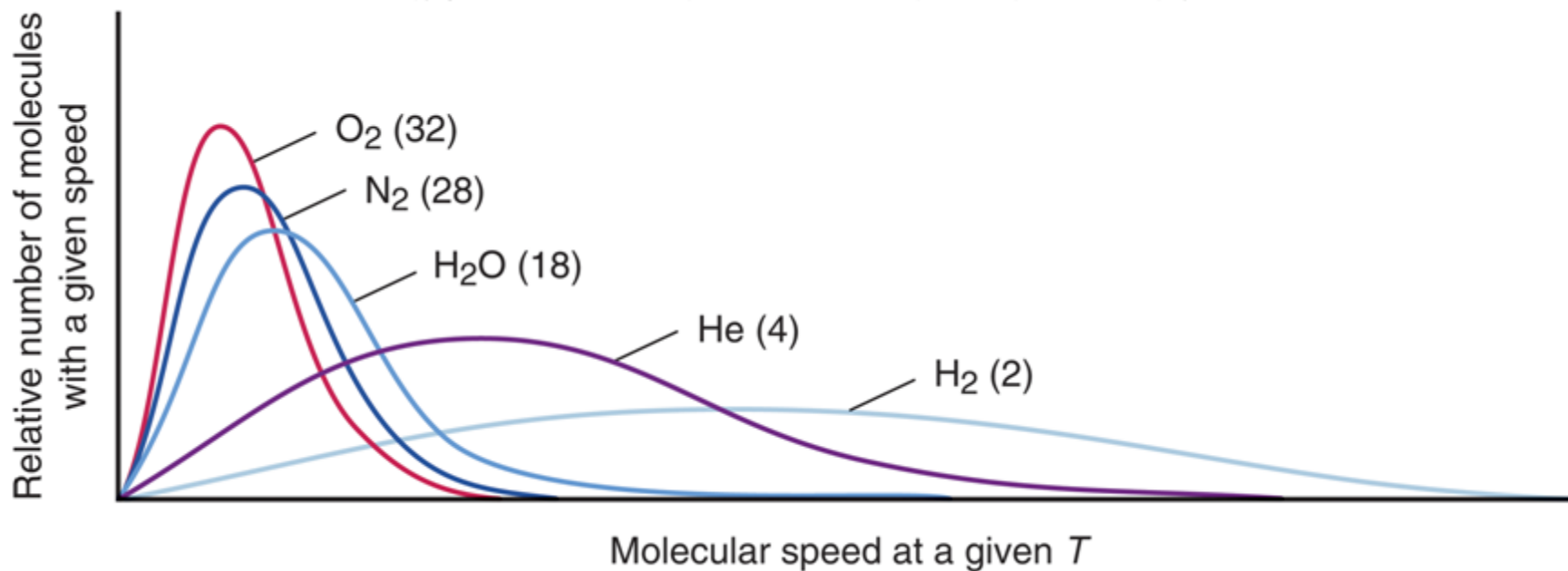
Kinetic energy depends on both the mass and the speed of a particle.

At the same T , a heavier gas particle moves more slowly than a lighter one.



Figure 5.19 The relationship between molar mass and molecular speed.

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Graham's Law of Effusion

Effusion is the process by which a gas escapes through a small hole in its container into an evacuated space.

Graham's law of effusion states that the rate of effusion of a gas is inversely proportional to the square root of its molar mass.

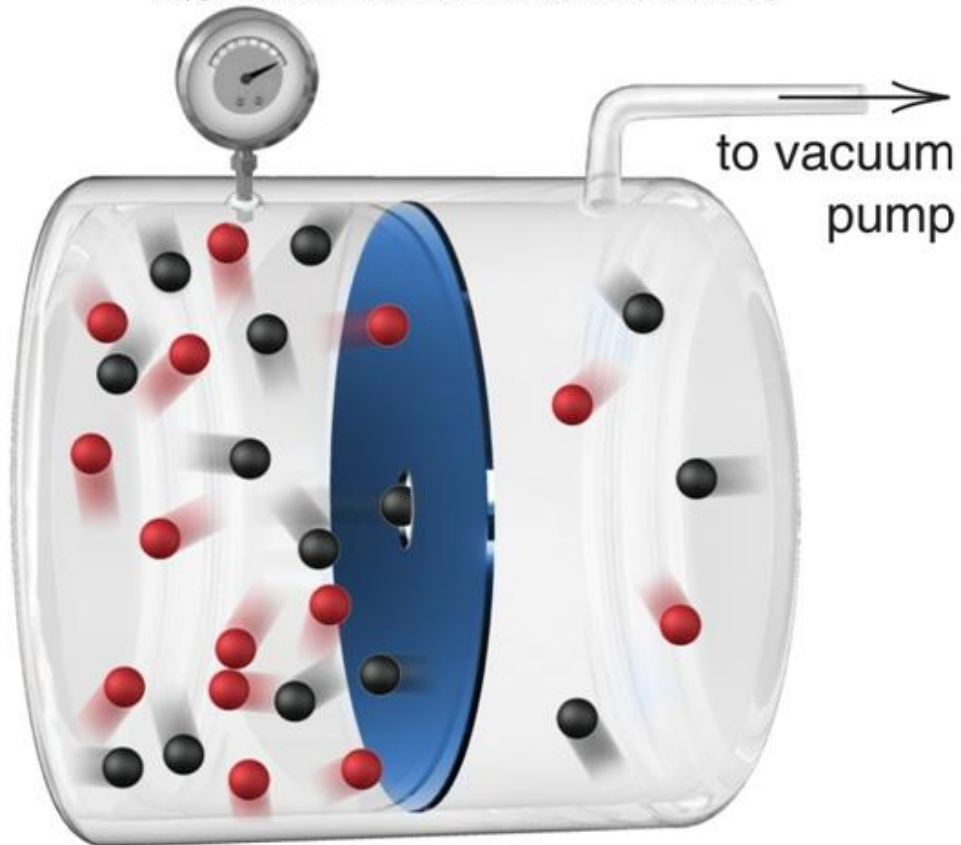
A lighter gas moves more quickly and therefore has a higher rate of effusion than a heavier gas at the same T .

$$\text{Rate of effusion} \propto \frac{1}{\sqrt{\mathcal{M}}}$$



Figure 5.20 Effusion. Lighter (*black*) particles effuse faster than heavier (*red*) particles.

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Sample Problem 5.13

Applying Graham's Law of Effusion

PROBLEM: A mixture of helium (He) and methane (CH₄) is placed in an effusion apparatus. Calculate the ratio of their effusion rates.

PLAN: The effusion rate is inversely proportional $\sqrt{\mathcal{M}}$ for each gas, so we find the molar mass for each substance using its formula and take the square root. The ratio of the effusion rates is the inverse of the ratio of these square roots.

SOLUTION: \mathcal{M} of CH₄ = 16.04 g/mol \mathcal{M} of He = 4.003 g/mol

$$\frac{\text{rate He}}{\text{rate CH}_4} = \sqrt{\frac{16.04}{4.003}} = \boxed{2.002}$$



Real Gases: Deviations from Ideal Behavior

- The kinetic-molecular model describes the behavior of ideal gases. Real gases deviate from this behavior.
- Real gases have real volume.
 - Gas particles are **not** points of mass, but have volumes determined by the sizes of their atoms and the bonds between them.
- Real gases do experience attractive and repulsive forces between their particles.
- Real gases deviate most from ideal behavior at ***low temperature*** and ***high pressure***.



**Table 5.3 Molar Volume of Some Common Gases at STP
(0°C and 1 atm)**

Gas	Molar Volume (L/mol)	Boiling Point (°C)
He	22.435	-268.9
H ₂	22.432	-252.8
Ne	22.422	-246.1
Ideal gas	22.414	-
Ar	22.397	-185.9
N ₂	22.396	-195.8
O ₂	22.390	-183.0
CO	22.388	-191.5
Cl ₂	22.184	-34.0
NH ₃	22.079	-33.4



Figure 5.21

Deviations from ideal behavior with increasing external pressure

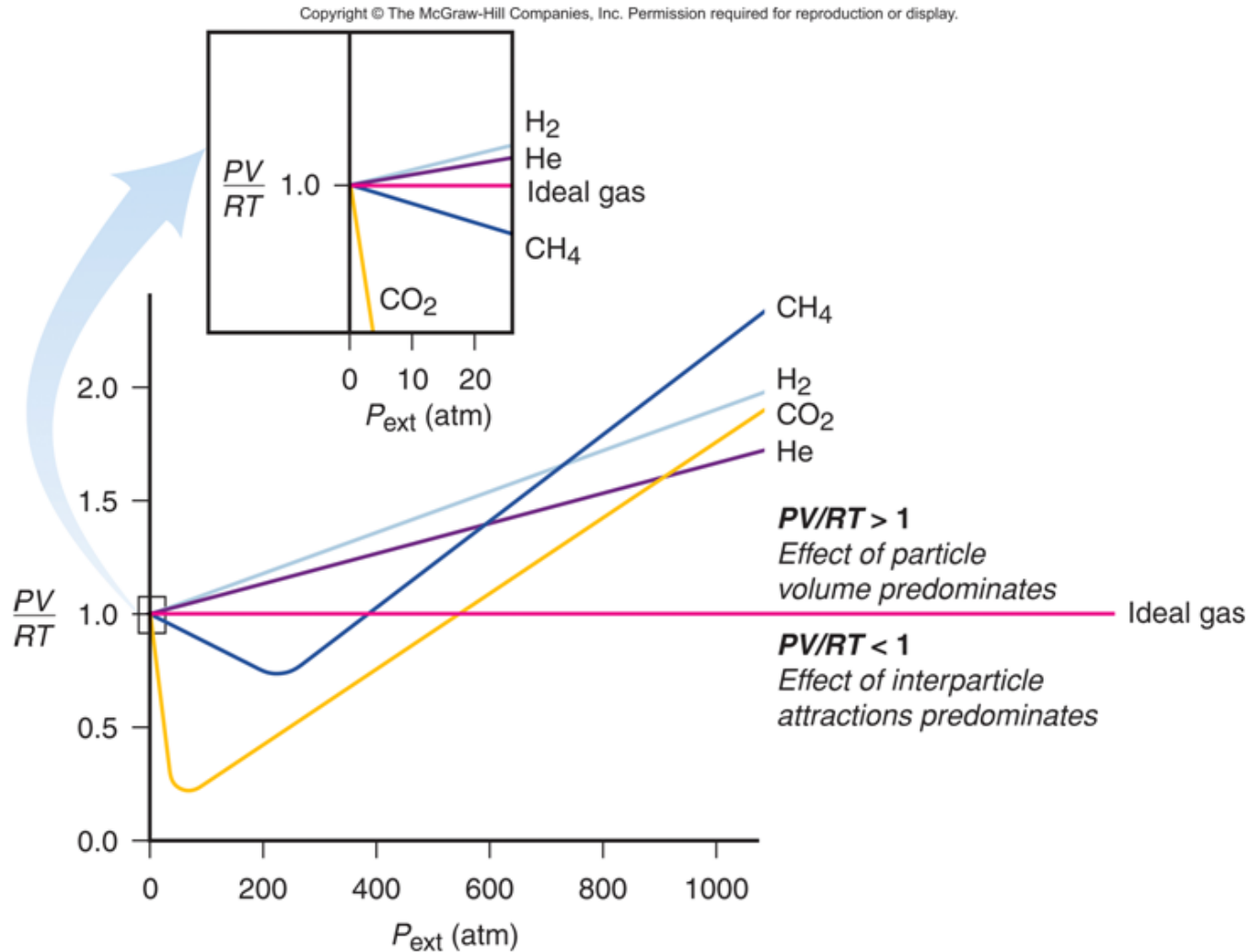


Figure 5.22

The effect of interparticle attractions on measured gas pressure.

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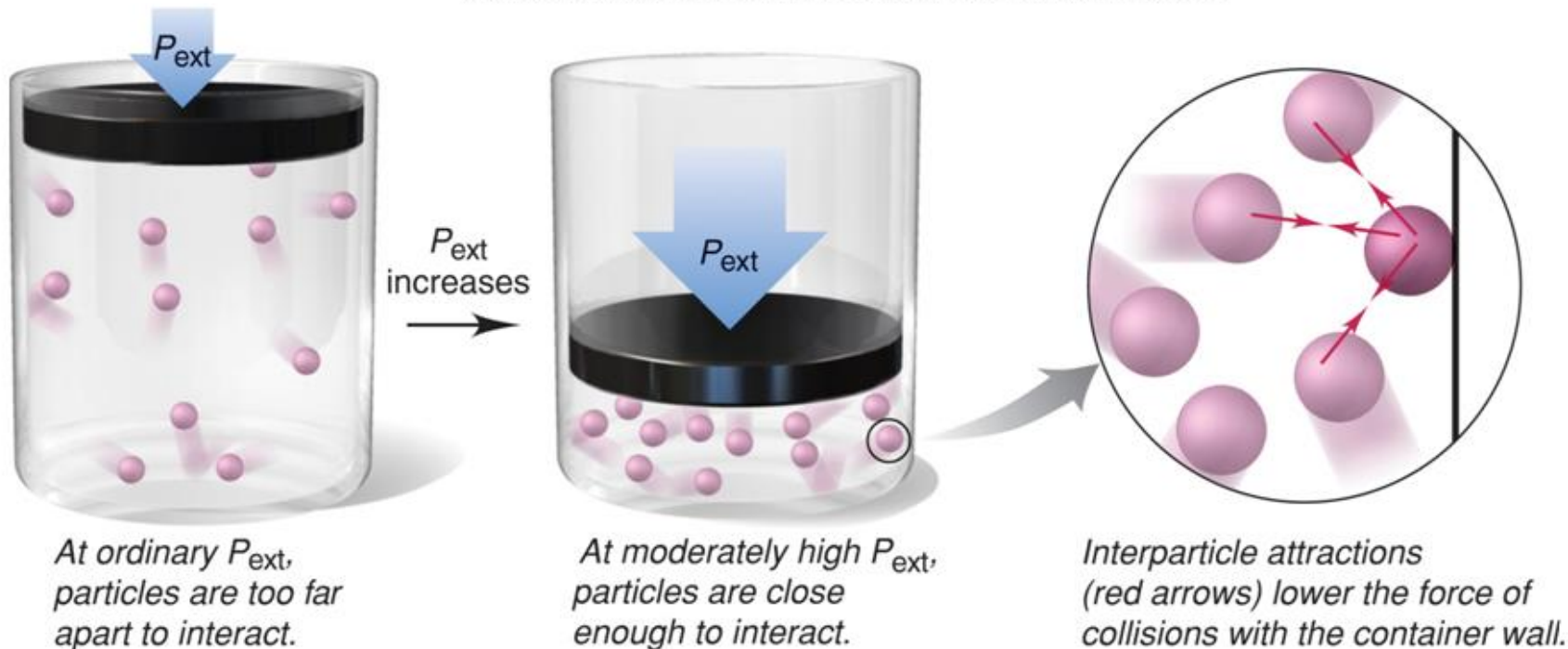
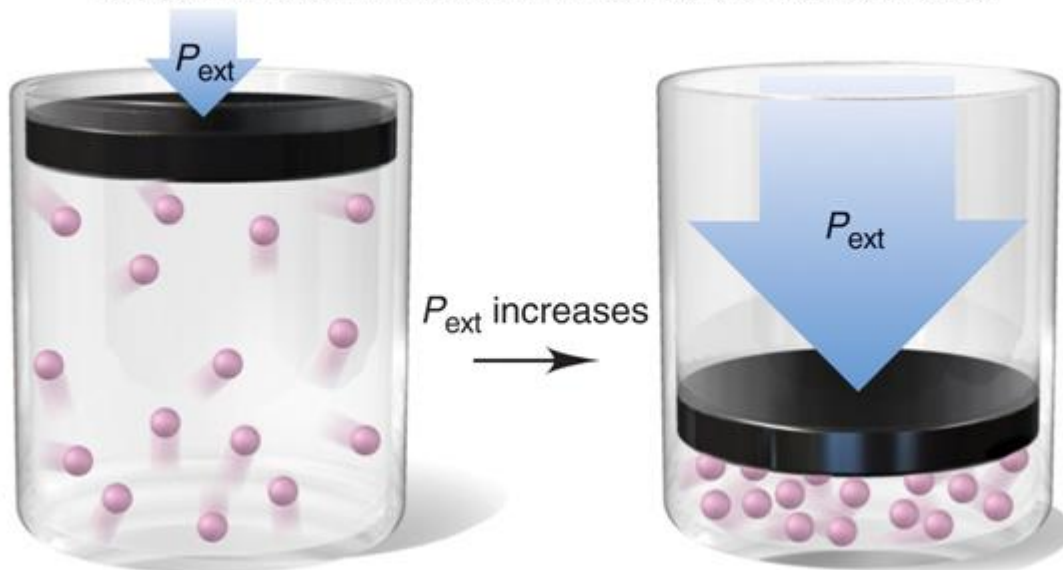


Figure 5.23 The effect of particle volume on measured gas volume.

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At ordinary P_{ext} , free volume \approx container volume because particle volume is an insignificant portion of container volume.



At very high P_{ext} , free volume $<$ container volume because particle volume becomes a significant portion of container volume.



The van der Waals equation

- The van der Waals equation adjusts the ideal gas law to take into account
 - the real volume of the gas particles and
 - the effect of interparticle attractions.

Van der Waals
equation for n
moles of a real gas

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

The constant a relates to factors that influence the attraction between particles.

The constant b relates to particle volume.



Table 5.4 Van der Waals Constants for Some Common Gases

Gas	$a \left(\frac{\text{atm}\cdot\text{L}^2}{\text{mol}^2} \right)$	$b \left(\frac{\text{L}}{\text{mol}} \right)$
He	0.034	0.0237
Ne	0.211	0.0171
Ar	1.35	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0511
H ₂	0.244	0.0266
N ₂	1.39	0.0391
O ₂	1.36	0.0318
Cl ₂	6.49	0.0562
CH ₄	2.25	0.0428
CO	1.45	0.0395
CO ₂	3.59	0.0427
NH ₃	4.17	0.0371
H ₂ O	5.46	0.0305

